

Effects of T , fO_2 , and doping level on diffusion of HFSE in rutile

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The mineral rutile is a common accessory phase in high-grade metamorphic rocks, and has gained increasing importance in the geosciences as a recorder of tectonic processes, as a single-mineral thermometer, a geochronometer, a geospeedometer, and as a provenance indicator. Apart from the growing interest of the geological community in rutile, there is an even greater demand by material scientists for quantitative data on trace-element incorporation (impurities and doping), defect structure, and diffusion in rutile.

We performed diffusion experiments using thin-film couples on synthetic rutile for Zr, Hf, Nb and Ta parallel to the a- and c-axes at temperatures between 800 and 1100 °C and a range of fO_2 between air and 10^{-13} Pa (i.e., $\log fO_2 = IW-3.5$). Diffusion couples were analysed using SIMS depth profiling [1].

Diffusion coefficients D for HFSE were found to be concentration dependent above a threshold of $\approx 1000 \mu\text{g/g}$, but not at lower concentrations. At constant fO_2 the temperature dependence of D follows an Arrhenius function in the temperature range investigated, and D decreases in the order $D_{\text{Nb}} \approx D_{\text{Zr}} \approx 2 D_{\text{Hf}} \approx 10 D_{\text{Ta}}$. This entails a strong diffusive fractionation of Nb/Ta consistent with earlier studies [1], but only a minor effect on Zr/Hf. A systematic dependence of diffusion of all four elements on fO_2 was found for low fO_2 ($\leq \text{FMQ}$), which is similar to that found for self diffusion of Ti. Our experimental results are in very good agreement with earlier radio-tracer experiments for Zr diffusion in rutile [2].

Equilibrium concentrations of the relevant point defects calculated based on available thermodynamic data reproduce the observed effects of fO_2 and heterovalent substitutions such as Nb^{3+} on the Ti site for the diffusion of HFSE. We illustrate that above a critical concentration (depending on T and fO_2) the respective diffusion coefficient is strongly reduced. The effect of fO_2 as well as the doping effect of Nb may, at least in part, explain the apparent discrepancies between this data set (together with [2]) and that of [3].

[1] Marschall et al. (2013), *EPSL* 375: 361–371; [2] Sasaki et al. (1985) *J. Phys. Chem. Solids*, 46: 1267–1283. [3] Cherniak et al. (2007), *EPSL*, 261: 267–279.